
TECHNICAL REPORT R-68

THE INTERACTIONS BETWEEN NITROGEN AND OXYGEN MOLECULES

By WILLARD E. MEADOR, JR.

**Ames Research Center
Moffett Field, Calif.**

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SUMMARY

A mathematical analysis is given of the delta function model for atomic interactions for the purposes of (1) establishing conditions for which the procedure is applicable, and (2) obtaining physical insight into the reasons why the method, simple though it is, yields potential curves which are in such good agreement with experimental data. Lippincott's original model is then extended to include the different effects of K- and L-shell electrons in molecular bond (or antibond) formation, and a screening-dependent parameter is introduced in the expression for the delta function strength. In addition, modifications are made which make the model more general in application—in particular, in regard to heteronuclear molecules.

Modified versions of the delta function model, together with general valence bond and molecular orbital theories and a reasonably extensive treatment of resonance, dispersion, and configuration interaction phenomena, are applied to selected excited states of the N_2 , NO, and O_2 molecules. The results, in conjunction with known spectroscopic data and/or calculations of the ratios of exchange integrals, are then used to find curves representing N_2-N_2 , N_2-O_2 , and O_2-O_2 interactions, chosen because of their importance in problems of aerophysics. Although the absolute accuracy of the latter potentials is difficult to ascertain, they are at least consistent with available scattering and viscosity measurements. This is especially true of the N_2-N_2 calculation in which remarkable agreement with scattering experiments is obtained. It is further believed that the points covered in this paper will prove useful in future investigations of the interactions between ions and neutral species.

INTRODUCTION

Interactions between oxygen and nitrogen molecules are of fundamental importance in the study of atmospheric transport properties and other phenomena associated with man's venture into space (ref. 1). As a first step in the theoretical investigation of scattering cross sections, for example, it is necessary to have a fairly detailed knowledge of the functional form of the interaction potentials between the elements of the gas under consideration. However, the standard methods of molecular quantum mechanics (e.g., the Heitler-London (ref. 2) and molecular orbital (ref. 3) approaches), in spite of the very lengthy mathematical procedures involved, do not result in sufficiently accurate curves for quantitative analysis. It is therefore necessary to develop new techniques for the calculation of these curves or else resort to their determination from experimental scattering and viscosity data. The latter can be extremely difficult and, while acceptable as far as the end result is concerned, is certainly not as satisfying to the theorist as is the former.

Mason and Vanderslice (ref. 4) have recently presented a method for the calculation of intermolecular forces using a one-dimensional model in which the nuclear-electronic coulomb potentials are replaced by delta functions. Thus far, most of the applications of this model have been made on such simple systems as hydrogen (ref. 5) and rare gas atoms (ref. 4) because of the spherical symmetry and closed electron shells, which imply only one possible interaction curve. The results are in surprisingly good agreement with experimental data in view of the simplicity of the assumptions involved.

Despite this success, however, it has been generally conceded that the model is really only semiempirical and that a cancellation of errors plays a large part in the results. The purpose of the present paper is fourfold as follows:

1. To analyze the delta-function model and show why it works.
2. To apply modified versions of the model to N_2-N_2 , N_2-O_2 , and O_2-O_2 interactions. The first example is used to iron out many of the procedural difficulties and is chosen because of the chemical similarity of molecular nitrogen to the rare gas atoms. Also experimental scattering data exists for this case.
3. To investigate the effects of a variable screening parameter.
4. To investigate the importance of dispersion forces, especially in regard to their short-range cut-off behavior.

LIST OF SYMBOLS

a	radius of the outermost electronic shell in an atom	O	symbol for atomic oxygen; also an atomic orbital centered on oxygen when used with the subscript x , y , or z
a, A, B, c, d	constants which appear in the approximate wave functions and interaction potentials	p	exponent defined in connection with the delta function strength
a, b	coefficients of linear combination of atomic orbitals	P	probability of the resonance state O^+-N^-
c	variable used in the delta function model and related to the atomic energies at infinite internuclear separation	r	distance of an electron from its own nucleus; also interatomic separation
d	molecular bond length	R	distance between centers of mass of molecules
E	energy	R_m	position of Van der Waals minimum
g	delta function strength	S_{ij}	overlap integral between atomic orbitals i and j centered on different atoms
H	total Hamiltonian operator	V	potential of electron; also interaction potential for diatomic molecules as defined in text
I	atomic ionization potential	V_o	constant which appears in the exponential curve fit of several interaction potentials
I_H	ionization potential of atomic hydrogen	x, y, z	Cartesian coordinates of an atomic electron; also variables defined in connection with the overlap integrals
I_{Li}	ionization potential of atomic lithium	Z	effective nuclear charge of L-shell electrons
J_{ij}	exchange integrals between atomic orbitals i and j on different atoms	α	parameter in the modified Buckingham empirical function
k	ratio of squares of overlap integrals; also resonance parameter	α, β	spin functions
n	number of effective electron pairs in a diatomic molecule	β	parameter in the Hulburt-Hirschfelder empirical function
N	symbol for atomic nitrogen; also an atomic orbital centered on nitrogen when used with the subscript x , y , or z	γ	variable related to the resonance parameter
		ϵ	half width of square well potential (approaches zero to form delta function); also depth of Van der Waals minimum
		λ	resonance parameter
		μ, ν, φ	elliptical coordinates
		ρ	distance between delta function centers
		τ	volume element ($d\tau$)
		Φ	interaction potential between molecules
		Φ'	interaction potential between molecules as obtained from an exponential curve fit
		ψ	wave function (subscripts o and n signify ground and n th excited states, respectively)

ω frequency of cosine wave function (see eq. (4b))

Energies are given in units of twice the ionization potential of atomic hydrogen, or in electron volts, as noted. Distances are given in units of first Bohr radius of atomic hydrogen, or in angstroms, as noted.

THE DELTA-FUNCTION MODEL

HYDROGEN-LIKE ATOMS

The wave equation for a ground state hydrogen-like atom is, in atomic units,

$$-\frac{1}{2r^2} \left[\frac{d}{dr} \left(r^2 \frac{d}{dr} \right) + 2Zr \right] \psi_0 = E_0 \psi_0 \quad (1a)$$

where

$$E_0 = -\frac{Z^2}{2}, \quad \psi_0 = \left(\frac{Z^3}{\pi} \right)^{1/2} e^{-Zr} \quad (1b)$$

and Z is the atomic number of the nucleus.

Now, considering the application of the Laplacian operator in Cartesian coordinates to ψ_0 , we obtain

$$\frac{\partial^2 \psi_0}{\partial x^2} = \left(\frac{Z^2 x^2}{r^2} + \frac{Z x^2}{r^3} - \frac{Z}{r} \right) \psi_0 \quad (2a)$$

and

$$-\frac{1}{2} \nabla^2 \psi_0 = -\frac{1}{2} \left(Z^2 + \frac{Z}{r} - \frac{3Z}{r} \right) \psi_0 = \left(-\frac{Z^2}{2} + \frac{Z}{r} \right) \psi_0 \quad (2b)$$

It is apparent then that the simple mathematical procedure of reducing the problem to one dimension by taking the components y and z to be zero in ψ_0 and equation (2a) results in

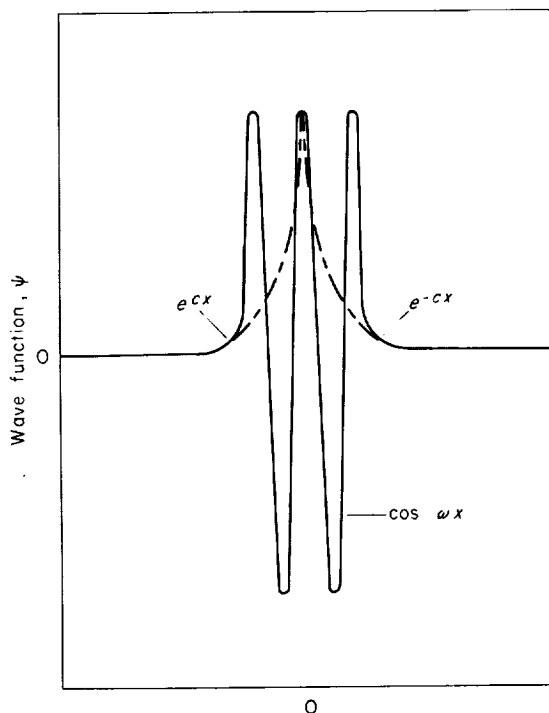
$$\frac{d^2 \psi_0}{dx^2} = \left(Z^2 + \frac{Z}{|x|} - \frac{Z}{|x|} \right) \psi_0 \quad (3a)$$

or

$$-\frac{1}{2} \frac{d^2 \psi_0}{dx^2} = -\frac{Z^2}{2} \psi_0 \quad (3b)$$

This last equation is obviously equivalent, at least insofar as the mathematical eigenvalue problem is concerned, to equation (1a) but with the very important physical exception that a potential energy function is not included. The fortuitous cancellation of the second and third terms on the right-hand side of equation (3a)

is the crux of the simplification with the result that the wave function of the atom may be represented in one dimension by the dotted curves shown in sketch (a).



Sketch (a).—The hydrogen atom wave function in the delta-function model.

The correct excited state energies are also easily obtainable from equation (3b) by simply using $\psi_n = \exp(-Z|x|/n)$, where n is the principal quantum number; however, the situation tends to become more obscure and further removed from physical reality because of the fact that the true wave functions are not simple exponentials.

Since it seems possible to get along so well without worrying about a potential energy function in the one-dimensional Hamiltonian, the question might reasonably be asked, at this point, as to why Mason and Vanderslice (ref. 4) bother about introducing a square well at the position of the nucleus and then letting the width of this well approach zero and its depth approach infinity in such a way as to degenerate into a delta function, especially since the correct energy values are obtained without doing this and the model is but a mathematical construct. The answer is that in order to apply the method to the more

complicated cases of molecules, it will be necessary at least that the equations represent some sort of physical situation, even though it might not be that of an atom, and that they satisfy the boundary conditions of general quantum theory. It is quite apparent that the latter condition is not fulfilled in the above simplified model from the mere fact that the slope of the wave function is not continuous at the origin, an observation which clearly indicates a potential center at this point.

A possible procedure for circumventing the above difficulty is to connect the two exponential regions (i.e., $\exp(cx)$ for $x < 0$ and $\exp(-cx)$ for $x > 0$) with a suitable even function of x , such that the slopes are continuous, and then to find the corresponding potential from which it can originate. Perhaps the simplest such connecting function is the cosine, the frequency of which may be allowed to approach infinity, and which is the wave function of a particle in a one-dimensional box—hence the use of the delta function type of potential (see sketch (a)). It follows then that while the delta functions associated with two such atoms cannot, of course, overlap, the corresponding wave functions can. The situation for the individual atom is, in some respects, similar to the "tunnel effect" in the α decay of radioactive nuclei.

In other words, consider the x axis to be divided into three regions with the following set of wave functions and potentials:

$$\psi_I = A \exp(cx), \quad V = 0 (x \leq -\epsilon) \quad (4a)$$

$$\psi_{II} = B \cos \omega x, \quad V = -V_o (-\epsilon \leq x \leq \epsilon) \quad (4b)$$

$$\psi_{III} = A \exp(-cx), \quad V = 0 (x \geq \epsilon) \quad (4c)$$

where c is essentially an effective nuclear charge and is equal to $(-2E)^{1/2}$ in this problem. The parameter ω is determined in such a fashion as to satisfy the one-dimensional wave equation, including the delta-function potential, and 2ϵ represents the width of the square well. Thus

$$-\frac{1}{2} \frac{d^2}{dx^2} (\cos \omega x) + V \cos \omega x = E \cos \omega x \quad (5a)$$

or

$$\omega^2 = 2(E - V) = 2(E + V_o) = -c^2 + 2V_o \quad (5b)$$

The quantity ω must be real, of course, otherwise ψ_{II} would be a hyperbolic function.

Now V_o may be obtained from the requirement that the functions and their first derivatives join smoothly at the boundaries of the regions, that is,

$$\psi_I = \psi_{II}, \quad \psi_I' = \psi_{II}' \quad \text{at } x = -\epsilon \quad (6a)$$

$$\psi_{II} = \psi_{III}, \quad \psi_{II}' = \psi_{III}' \quad \text{at } x = \epsilon \quad (6b)$$

This results in $\omega \tan \omega \epsilon = c$ and, since ϵ may be allowed to approach zero without loss of generality for purposes of simplification, we have

$$\omega^2 \epsilon = -c^2 \epsilon + 2V_o \epsilon = c \quad (7a)$$

Letting $g = c + c^2 \epsilon$, this yields

$$V_o = \frac{g}{2\epsilon}, \quad \omega^2 = -c^2 + \frac{g}{\epsilon} \quad (7b)$$

In this example, $g \approx c$, but this is not necessarily true in the case of molecules. This point will become clearer in a subsequent section of the report on H_2^+ .

It should be noted here that the shrinking of the width (2ϵ) of the potential well to zero automatically leads to the increase of the depth ($g/2\epsilon$) to infinity, but in such a way that the product of width and depth is equal to g , a finite number. Thus, the potential used here is indeed a delta function of strength g ; however, it is in no way unique, that is, this is not the only way in which a one-dimensional analysis can be made physically plausible.

Finally, it must be remembered in what follows that, when use is made of this model, no coulombic interaction of any kind appears explicitly in the Hamiltonian operator of an atomic system. Therefore, as follows from the first-order nature of this procedure, induction and other second-order effects must be added arbitrarily in order to obtain a complete description of forces between two or more interacting species. Moreover, any analysis involving a three-dimensional quantity, for example, angular momenta different from zero and their interactions with spin resulting in fine structure corrections, must be handled in a somewhat different manner. The loss of this type of general physical insight, however, is not an uncommon occurrence when mathematical simplifications are made for the purpose of dealing with a more specific effect.

THE H_2^+ AND H_2 MOLECULES

Following Lippincott's (ref. 5) method of bringing two delta-function atoms together to form a delta-function molecule, we may divide the x axis into five regions with the following wave functions:

$$\psi_I = A e^{cx} \quad \left(x \leq -\frac{\rho}{2} - \epsilon\right) \quad (8a)$$

$$\psi_{II} = B_1 \cos \omega x \quad \left(-\frac{\rho}{2} - \epsilon \leq x \leq -\frac{\rho}{2} + \epsilon\right) \quad (8b)$$

$$\psi_{III} = D[\exp(-cx) + \exp(cx)] \quad \left(-\frac{\rho}{2} + \epsilon \leq x \leq \frac{\rho}{2} - \epsilon\right) \quad (8c)$$

$$\psi_{IV} = B_2 \cos \omega x \quad \left(\frac{\rho}{2} - \epsilon \leq x \leq \frac{\rho}{2} + \epsilon\right) \quad (8d)$$

$$\psi_V = A e^{-cx} \quad \left(x \geq \frac{\rho}{2} + \epsilon\right) \quad (8e)$$

where ρ is the distance between delta-function centers. The positive sign is used in ψ_{III} to make the wave function symmetric in an interchange of nuclei, since, by general molecular orbital theory, this corresponds to a concentration of probability density in the region between nuclei and leads, therefore, to the lowest energy.

Using equation (7b) and applying the appropriate boundary conditions to the region end-points results in the equations

$$E = -\frac{c^2}{2} \quad (9a)$$

$$c = g(1 + e^{-c\rho}) \quad (9b)$$

$$E = -\frac{g^2}{2} (1 + e^{-c\rho})^2 \approx -\frac{g^2}{2} (1 + 2e^{-c\rho}) \quad (9c)$$

Equations (9b) and (9c) may now be solved simultaneously to determine c and E as a function of the delta-function separation ρ . The parameter g is, of course, determined simply by the requirement that the energy approach the correct isolated atom energies as ρ goes to infinity ($g=1$ for H_2^+ and $2^{1/2}$ for H_2).

Lippincott now makes the further argument that the approximation should be considerably improved by using "floating" delta functions, that is, by allowing the delta function centers to

be shifted off the nuclear centers. This procedure will clearly enable the charge distribution to be more concentrated in the region between nuclei ($\rho < r = \text{internuclear separation}$) in the case of bond formation and in the regions outside of the nuclei ($\rho > r$) in the case of repulsive states. This is essentially equivalent to the shifted atomic orbital procedure as applied to H_2 by Gurnee and Magee (ref. 6) and to H_3 by Meador (ref. 7), and it is also similar to second-order perturbation theory in which, for example, hybrid $1s$ and $2p$ orbitals are used for H_2 in the ground state (ref. 8). The methods for specifying ρ as a function of r will become apparent in the next section.

THE ${}^7\Sigma_u^+$ EXCITED STATE OF N_2

In a recent paper Vanderslice, Mason, and Lippincott (ref. 9) applied the delta-function model to the calculation of the energy of the ${}^7\Sigma_u^+$ state of N_2 , in which all the valence electrons are unpaired. The antisymmetric wave functions appropriate to repulsive states were used in place of the symmetric ones discussed previously and resulted in the equations

$$c = g(1 - e^{-c\rho}) \quad (10a)$$

$$E = -\frac{ng^2}{2} (1 - 2e^{-c\rho}) \quad (10b)$$

where n is the number of electron pairs (seven in this case). The assumption is made that the many electrons may be replaced by a single effective charge distribution; more precisely, the total interaction energy consists of n times the average interaction energy of all pairs of electrons, as for two hydrogen atoms.

The interaction energy may now be expressed as

$$V(r) = E(r) - E(\infty) = ng^2 e^{-c\rho} \quad (11)$$

where

$$\rho = r + 2ac^{-1/a} \quad (12)$$

This last equation is merely a simple way to satisfy the requirements:

$$(a) \quad \rho > r \text{ (repulsive state)}, \quad \rho \rightarrow r \quad \text{as } r \rightarrow \infty$$

$$(b) \quad \rho(r=0) = 2a, \text{ where } a \text{ is the average radius of the outermost electronic orbit of an isolated atom } (a=0.56 \text{ \AA} \text{ (ref. 10) for nitrogen)—the "united atom."}$$

With the idea that the delta-function strength (g) may be regarded as proportional to the ionization potential of an isolated atom, as implied by the earlier scattering investigations of Bloch for heavy targets (ref. 11), one obtains

$$g=2(I_H)^{1/2} \left(\frac{I}{I_H} \right) = 2^{1/2} \left(\frac{I}{I_H} \right) \quad (13)$$

where I and I_H are the ionization potentials of atomic nitrogen and hydrogen, respectively. This procedure finally yields a potential energy which can be represented by the expression

$$V(r)=317.8 \exp(-2.753 r) \quad (14)$$

where r is measured in angstroms, and V is in electron volts.

The present paper is an extension of the above work in that allowances are made for the smallness of the contributions of the inner or K-shell electrons to the repulsive forces between atoms (or to bond formation in the case of bound states). The question is raised also as to whether the delta-function strength should be proportional to I or to $I^{1/2}$, or perhaps to some power in between, especially in view of the fact that equation (13) signifies a discontinuity in going from hydrogen ($g \sim I^{1/2}$) to a more complicated atom ($g \sim I$). As a more natural assumption, the introduction of a variable parameter in order to make this transition less abrupt seems appropriate. In addition, since there are only five L-shell electron pairs involved in N_2 , it is expected that the final form for g should more closely resemble that for hydrogen than for the heavy atoms.

The first extension involves a comparison with lithium instead of hydrogen in the equation for g . In this case the following system of equations results (energy in electron volts, and r in angstroms):

$$\rho = \frac{r}{0.5292} + 2.1164 e^{-r/0.56} \quad (15a)$$

$$g = 2 \left(\frac{I_{Li}}{27.206} \right)^{1/2} \left(\frac{I}{I_{Li}} \right)^p = 2 \left(\frac{5.363}{27.206} \right)^{1/2} \left(\frac{14.48}{5.363} \right)^p \quad (15b)$$

$$c = g(1 - e^{-c\rho}) \quad (15c)$$

$$V(r) = 5(27.206)g^2 e^{-c\rho} = 136.03g^2 e^{-c\rho} \quad (15d)$$

where p is a number, to be determined, between one-half and unity.

A comparison of this approach with experimental data will be given below, where it is shown that $p=1/2$ gives very good results. This corresponds to $g=2(I/27.206)^{1/2}$ so that the interaction energy may be represented (after some manipulation using Newton's iteration procedure and curve fitting) by the expression

$$V(r) = 253.9 \exp(-2.716r) \text{ ev} \quad (16)$$

It should be noted here that the method of approximation of perfect pairing, as employed in subsequent sections of this report, involves only $2p$ type electrons in a description of interatomic forces. For this reason, it perhaps would have been more consistent to have considered three electron pairs in equation (15d), instead of five, and to have used boron, instead of lithium, in equation (15b). The above treatment emphasizes the shell structure, and hence regards only the two $1s$ electrons as being transnuclear, whereas the latter points out the division into subshells and is used only in finding relationships between energy states.

Equations (15) point out clearly the advantages of using the delta-function model, at least from the standpoint of mathematical simplicity, since the wave equation becomes completely separable in the electron coordinates, and complicated coulomb and exchange integrals, etc., do not enter the picture.

THE N_2 - N_2 INTERACTION

The approximation of perfect pairing (ref. 12) describes the interaction between two nitrogen molecules as simply the sum of four atomic interactions. In the case of neutral species (i.e., neglecting any ionic contributions due to resonance) the interaction potential is thus given by a particular sum of exchange integrals as follows:

$$V = \sum_1 J_{ij} - \sum_2 J_{ij} - \frac{1}{2} \sum_3 J_{ij}$$

where

\sum_1 the sum over orbitals with paired spins (anti-parallel)

\sum_2 the sum over orbitals with parallel spins

\sum_3 the sum over orbitals with nonpaired or random spins

The choice of coefficients, of course, follows directly from simple valence bond theory. For example, the factor $-\frac{1}{2}$ in the last term is a consequence of the fact that this represents a completely random situation and the degeneracies of paired and parallel spin states are one and three, respectively. The exchange energy is, therefore, $(\frac{1}{4}-\frac{3}{4})J_{ij}=-\frac{1}{2}J_{ij}$.

Further assumptions concerning molecular interactions are:

1. The exchange integrals are essentially the same as would prevail if the atoms were isolated instead of being members of molecules. The directions of the distortions experienced by the electronic charge distributions as the molecules approach each other certainly tend to make this approximation good and, in any case, the error introduced is probably very small for the distances under consideration (2.4 to 3.2 Å).
2. The resonance contribution is insignificant because of the small electron affinity of molecular nitrogen. In many respects N_2 behaves like an inert gas atom so that N_2^- is extremely unlikely.
3. Only the valence $2p_x$, $2p_y$, and $2p_z$ atomic orbitals are considered as contributing to the exchange forces between atoms.
4. The coulomb interaction between neutral molecules is negligible at fairly large internuclear separation in comparison with the exchange forces.
5. Only one N_2-N_2 interaction curve is considered to be of importance, that is, the possibility of chemical reaction is ignored. The \sum_u^+ state of N_2 may now be represented by

$$V(r) \approx -(J_{xx} + J_{yy} + J_{zz}) \quad (17)$$

and the interaction between nitrogen atoms, either or both of which are members of molecules, by

$$V'(r) \approx -\frac{1}{2} (J_{xx} + J_{yy} + J_{zz}) \quad (18)$$

Combining equations (16), (17), and (18), we have

$$V'(r) \approx \frac{1}{2} V(r) = V_0 e^{-br} = 127.0 e^{-2.716r} \text{ ev} \quad (19)$$

The total interaction between two nitrogen

molecules is then given by the sum of the four interactions between their constituent atoms, four in all, and depends implicitly on their relative orientations. For comparison with experimental scattering and viscosity data, it is convenient to average geometrically (ref. 9) over all possible orientations, which yields for the average N_2-N_2 interaction

$$\Phi(R) = 4V_0 e^{-bR} (b^3 R d^2)^{-1} [2(bR+2)(\cosh bd - 1) - 2bd \sinh bd] - \frac{36.0}{R^6} \text{ ev} \quad (20)$$

where

R distance between the centers of mass of the molecules

d bond length of $N_2 = 1.094$ Å (ref. 13)

$-36.0/R^6$ London dispersion or second-order perturbation energy (ref. 14)

Calculated values of Φ from this equation and from

$$\Phi'(R) = A e^{-BR} - \frac{36.0}{R^6} \quad (21)$$

where $A=658.66$ and $B=2.630$ for $p=0.5$, as obtained from curve fitting, are presented in table I. Also shown is the energy for $p=0.6$ in order to show the trend when this parameter is varied.

Comparisons between the theoretical results of this paper and those of Vanderslice, Mason, and Lippincott (ref. 9), together with the experimental data of Amdur, Mason, and Jordan (scattering measurements, ref. 15) and Mason and Rice (viscosity measurements, ref. 16), are presented in table II and sketch (b). The excellent agreement would seem to justify the present approach.

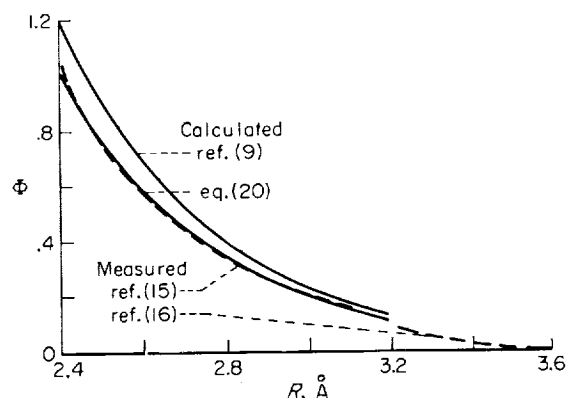
There is, however, a discrepancy at large R where the theoretical curve does not approach zero as rapidly as the viscosity data, but this may be due partly to the inadequacy of the experimental results in this region. It is also apparent

TABLE I. $-N_2-N_2$ INTERACTION ENERGIES

R	Eq. (20) and $p=0.6$	Eq. (20) and $p=0.5$	Eq. (21) and $p=0.5$
2.4	0.6272	1.0071	1.0080
2.5	.4637	.7726	.7723
2.6	.3411	.5911	.5905
2.7	.2494	.4508	.4507
2.8	.1812	.3429	.3432

TABLE II. COMPARISON OF N₂-N₂ INTERACTION ENERGIES

R	Calculated		Measured	
	Ref. 9	Eq. (21) and $p=0.5$	Ref. 15	Ref. 16
2.4	1.190	1.008	1.045	
2.5	.905	.772	.757	
2.6	.692	.591	.568	
2.7	.527	.451	.440	
2.8	.400	.343	.336	
2.9	.303	.261	.257	
3.0	.229	.198	.200	
3.1	.173	.149	.157	
3.2	.130	.112		0.093
3.3				.050
3.4				.023
3.5				.011
3.6				.005

Sketch (b).—Comparisons of N₂-N₂ interaction energies.

that the two theoretical curves converge at large distances because of the decreasing importance of distinguishing between K- and L-shell electrons. Finally, the fact that the curve of this paper lies below the one derived from scattering data for R less than about 2.45 is due primarily to the inability of the model to account for the strong repulsive forces encountered when the electronic charge distributions effectively overlap; that is, the diatomic theoretical curve for the ${}^7\Sigma_u^+$ excited state does not approach infinity at r equal to zero. The specific neglect of coulomb interactions in the Hamiltonian operator apparently is valid only when the intermolecular separation is large enough that the forces (other than exchange)

between individual particles cancel out. These arguments thus make clear the limitations of the delta-function simplification and point the way to the modifications necessary when one or both of the interacting species is an ion.

Finally, another lower limit on the distance between molecules, insofar as this theory is concerned, is the point at which the procedure of averaging over orientations becomes invalid. Such a point would correspond to a separation at least as great as $2(d/2)=1.094 \text{ Å}$.

DISPERSION FORCES

The discrepancy between theory and experiment at small R (sketch (b)) may, to a minor extent compared to the reasons stated in the preceding section, be ascribed to the poor expression for the dispersion term. The approximations involved in the derivation of this term are such that, in short-range interactions, it is usually better to neglect dispersion entirely in comparison with the first-order energies. For this reason it would probably have been more realistic to have omitted the term $-36.0/R^6$ in equations (20) and (21); however, because of its not insignificant contribution to the total energy ($-36.0/R^6$ varies from -0.188 at $R=2.4$ to -0.075 at $R=2.8$), an attempt must be made to compensate for the omission of the term by allowing the p of equation (15b) to be greater than 0.5.

The best agreement with experiment is obtained, and to this extent the entire procedure must be regarded as essentially semiempirical, if p is taken to be 0.55. The results are shown in table III, where column 2 values were calculated using equation (20) without dispersion and column 3

TABLE III. N₂-N₂ INTERACTION ENERGIES

R	Eq. (20) without dispersion and $p=0.55$	Eq. (22)	Eqs. (20) and (15d)	Eq. (21) and $p=0.5$	Ref. 15
2.4	1.000	1.003	0.989	1.008	1.045
2.5	.759	.759	.755	.772	.757
2.6	.575	.575	.575	.591	.568
2.7	.436	.435	.437	.451	.440
2.8	.330	.329	.332	.343	.336
2.9	.250	.249	.251	.261	.257
3.0	.189	.189	.190	.198	.200

corresponds to the associated exponential curve fit given by

$$\Phi'(R) = 800.52 \exp(-2.784R) \quad (22)$$

Column 4 of the same table results from using an equation of the form (15d) directly in the expression for $\Phi(R)$, instead of going through the intermediate step of equation (16), and the two remaining columns are reprints from table II for purposes of comparison. Thus, at least in the range $2.5 < R < 2.8$, this last description of the interaction does an even better job of matching the scattering data, as the average discrepancy between theory and experiment at the points cited is reduced from 0.014 to 0.004 ev. The inadequacy of scattering measurements apparently begins to take hold for R greater than approximately 2.9.

In addition, a graphically constructed connecting curve between the present theoretical results and those obtained from viscosity data could yield a valuable empirical determination of the effective reduction factor and short-range cutoff of the dispersion forces. This will be shown more clearly in connection with N_2-O_2 .

For further comparison with the work of Vanderslice, Mason, and Lippincott (ref. 9), a calculation of the interaction energy between nitrogen atoms and molecules was made using equations (15) in conjunction with $p=0.55$,

$$V'(r) \approx \frac{1}{2} V(\sum_u^+) = V_0 e^{-br} \quad (\text{cf. eq. (19)}) \quad (23)$$

and

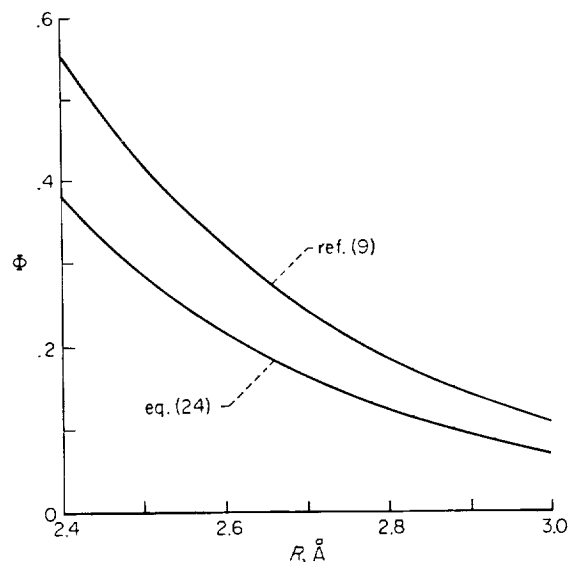
$$\Phi_1(R) = 2V_0 e^{-bR} (b^2 R d)^{-1} \left[2(bR+1) \sinh\left(\frac{bd}{2}\right) - 2\left(\frac{bd}{2}\right) \cosh\left(\frac{bd}{2}\right) \right] \quad (24)$$

Equation (24), of course, follows from the same type of averaging procedure as that used to obtain equation (20), and the intermediate stage of equation (16) was again omitted; that is, equation (23) was used for each value of R but no attempt was made to represent the entire range by a single exponential function.

The results are shown in table IV and sketch (c). There are, unfortunately, no experimental data available to check their validity. The Vander-

TABLE IV.—N—N₂ INTERACTION ENERGIES

R	Eq. (24)	Ref. 9
2.4	0.376	0.550
2.5	.285	.418
2.6	.215	.318
2.7	.163	.242
2.8	.123	.184
2.9	.092	.140
3.0	.070	.107



Sketch (c).—Comparisons of N—N₂ interaction energies.

slice, et al., (ref. 9) curve was calculated from

$$\Phi_1'(R) = 387.8 \exp(-2.733R) \quad (25)$$

To summarize, the exponential curve fit of equation (22) provides a very simple function for use as the repulsive part of the potential appearing in cross-section and transport integrals. The neglect of dispersion forces at large distances, however, prevents the usual potential minimum, which occurs at 5.160 Å as computed from equation (21) with the term $-36.0/R^6$. The corresponding value of the potential at this point is -0.0011 ev, whereas the Vanderslice, et al. (ref. 9), equations predict -0.0001 ev at 5.203 Å. On the other hand, in high-energy scattering experiments, the effect of this attractive contribution is often quite negligible and equation (20), without dispersion and without further modifications, should give very adequate results for this type of measurement.

INTERACTIONS BETWEEN NITROGEN AND OXYGEN

METHOD

For the interaction between nitrogen and oxygen atoms, both of which are members of their respective N_2 and O_2 molecules, the approximation of perfect pairing yields

$$V(r) = -\frac{1}{3} \left[2 \left(\frac{1}{2} \right) J_{xx} + \frac{1}{2} J_{yy} + \frac{1}{2} J_{zz} + \frac{1}{2} J_{xx} + 2 \left(\frac{1}{2} \right) J_{yy} + \frac{1}{2} J_{zz} + \frac{1}{2} J_{xx} + \frac{1}{2} J_{yy} + 2 \left(\frac{1}{2} \right) J_{zz} \right]$$

where the x axis is taken to coincide with the line of nuclear centers. Here again only p type atomic orbitals are considered and advantage has been taken of the small electron affinity of N_2 .

Since symmetry requirements dictate that J_{yy} is identical with J_{zz} , the above expression can be immediately reduced to

$$V(r) = -\frac{2}{3} (J_{xx} + 2J_{yy}) \quad (26)$$

In previous papers (refs. 9 and 17) employing this approach it has been customary to eliminate J_{xx} and J_{yy} from similar equations by using the same approximation of perfect pairing in connection with various states of associated diatomic molecules, the potential curves of which are obtained from spectroscopic data or by adopting the delta-function model. Such a procedure was particularly simple in the case of N_2-N_2 because of the almost trivial relation expressed in equation (19); in other words, only one diatomic state had to be considered and this was especially adaptable to a delta-function treatment. The present problem is considerably more complicated because of the following three major factors which enter into the nitric oxide calculation:

1. Any attempt to use a delta-function model must take into account the fact that there will be two different sets of delta-function strengths and "floating" parameters.
2. The appearance of four p electrons in atomic oxygen implies the existence of three-electron bonds or antibonds in the states of nitric oxide. Thus, a careful analysis of the approximation of perfect pairing, which works so well in the case of N_2 , becomes necessary.

3. The possible attachment of the "extra" oxygen electron to the nitrogen atom to form a resonance N^--O^+ state must also be considered.

The addition of an associated resonance parameter to the two unknown exchange energies in equation (26) requires a minimum of at least three independent relations to solve uniquely the N_2-O_2 problem. Unfortunately, only the $X^2\Pi$ ground state of nitric oxide is sufficiently stable to provide enough spectroscopic data for an application of the Rydberg-Klein-Rees semiempirical method (refs. 9 and 17).

In a recent paper by Vanderslice, Mason, and Maisch (ref. 17) these difficulties are more or less avoided by some arbitrary assumptions concerning the resonance phenomenon. In addition, a somewhat questionable method of obtaining the bound $^4\Pi$ state of NO, by using the spectroscopic constants of the corresponding state of O_2^+ in a Hulburt-Hirschfelder function, is employed. It is shown in the present work that a more consistent determination of the interaction potentials is obtained when a delta-function model is used to calculate the resonance parameter. A derived relation involving the ratio of exchange integrals, together with the aforementioned $X^2\Pi$ ground state data, is then sufficient to specify completely the molecular interaction.

THE RESONANCE PHENOMENON

As mentioned above, the ground state $X^2\Pi$ potential curve of nitric oxide has been calculated by Vanderslice and co-workers using the Rydberg-Klein-Rees semiempirical procedure. It has also been shown (ref. 17) that the long-range tail of this curve joins smoothly with the following Hulburt-Hirschfelder expression (ref. 18):

$$V(^2\Pi) = 6.609 [(1 - e^{-\beta})^2 + 0.06780 \beta^3 (1 + 2.663 \beta) e^{-2\beta} - 1] \quad \text{ev} \quad (27)$$

where

$$\beta = 3.1579 \left(\frac{r - 1.1508}{1.1508} \right)$$

and r is the distance between atoms (in angstroms).

If the customary molecular notation (ref. 13) is used, the configuration of the seven valence p electrons may be described by

$$(\sigma_x)^2 (\Pi_y)^2 (\Pi_z)^2 (\Pi_z^*)$$

where the molecular orbital wave functions are approximately given by

$$\Pi_z: aO_z + bN_z$$

$$\Pi_z^*: aO_z - bN_z, \text{ etc.}$$

and where a and b are coefficients of the linear combination of atomic orbitals. The O_z and N_z , of course, refer to $2p_z$ atomic orbitals centered on oxygen and nitrogen, respectively.

An application of the approximation of perfect pairing leads to $V(^2\Pi) = J_{xx} + J_{yy}$ plus the contribution from the remaining Π_z and Π_z^* molecular orbitals.

This last term, however, concerns three electrons, and the aforementioned simple theory is not adequate to describe such a situation. A very feasible extension has been suggested by Linnett (ref. 19) in terms of a mixture of atomic and molecular orbitals, which follows directly from the properties of matrices and determinants. The basis of this procedure is easily seen from a consideration of the case where one electron is in the Π_z orbital and another is in the Π_z^* orbital and where both have their spins in the same direction. The wave function for this two-electron problem is then given by

$$\begin{aligned} \psi &\sim \begin{vmatrix} \Pi_z(1)\alpha(1) & \Pi_z^*(1)\alpha(1) \\ \Pi_z(2)\alpha(2) & \Pi_z^*(2)\alpha(2) \end{vmatrix} \\ &= \begin{vmatrix} [aO_z(1) + bN_z(1)]\alpha(1) & [aO_z(1) - bN_z(1)]\alpha(1) \\ [aO_z(2) + bN_z(2)]\alpha(2) & [aO_z(2) - bN_z(2)]\alpha(2) \end{vmatrix} \end{aligned}$$

Adding the second column to the first, dividing by 2, subtracting the resulting first column from the second, and finally multiplying by $1/a$ and $-1/b$, gives, apart from a constant factor,

$$\psi \sim \begin{vmatrix} O_z(1)\alpha(1) & N_z(1)\alpha(1) \\ O_z(2)\alpha(2) & N_z(2)\alpha(2) \end{vmatrix}$$

In other words, in the description of these two electrons, it is irrelevant whether they are said to occupy the molecular orbitals or the corresponding atomic orbitals, that is, the contribution to $V(^2\Pi)$ is $-J_{yy}$ regardless of the viewpoint taken.

The remaining electron in the three-electron bond must, in order to satisfy the Pauli principle, have a spin function β and may roughly be con-

sidered as occupying the molecular orbital Π_z . But what is its contribution to the interaction potential? One might reasonably expect to find that since this single electron forms a one-electron bond, and since the strength of such a bond is usually about one-half that of the corresponding two-electron bond, a fairly good approximation ought to be

$$V(^2\Pi) = J_{xx} + \frac{1}{2} J_{yy}$$

This question will now be more thoroughly investigated in the light of the molecular orbital theory.

Using the ideas of Linnett and allowing the extra electron to be located either in Π_z or Π_z^* , we have for the three-electron wave function

$$\begin{aligned} \psi &\sim a \begin{vmatrix} O_z(1)\alpha(1) & N_z(1)\alpha(1) & O_z(1)\beta(1) \\ O_z(2)\alpha(2) & N_z(2)\alpha(2) & O_z(2)\beta(2) \\ O_z(3)\alpha(3) & N_z(3)\alpha(3) & O_z(3)\beta(3) \end{vmatrix} \\ &\quad \pm b \begin{vmatrix} O_z(1)\alpha(1) & N_z(1)\alpha(1) & N_z(1)\beta(1) \\ O_z(2)\alpha(2) & N_z(2)\alpha(2) & N_z(2)\beta(2) \\ O_z(3)\alpha(3) & N_z(3)\alpha(3) & N_z(3)\beta(3) \end{vmatrix} \end{aligned}$$

We expand these determinants and neglect the multiple exchange integrals giving rise to the possibility of all three electrons being exchanged between the two atoms. Such interaction terms are usually quite small in comparison with other contributions, as can be seen from overlap considerations. The interaction potential is then found to be

$$\begin{aligned} V &\approx -a^2(O_zN_z:O_zN_z:O_zO_z) - b^2(O_zN_z:O_zN_z:N_zN_z) \\ &\quad \pm 2ab(O_zO_z:N_zN_z:O_zN_z) \end{aligned}$$

where

$$\begin{aligned} (O_zN_z:O_zN_z:O_zO_z) &= \int [\dots O_z(1)O_z(2)O_z(3)]^* \\ &\quad H[\dots N_z(1)N_z(2)O_z(3)]d\tau, \text{ etc.} \end{aligned}$$

H is the Hamiltonian operator of the entire system, and the asterisk (*) signifies taking the complex conjugate.

In general, if O and N are taken to represent symbolically any two atoms, there are two extreme

cases to consider as follows:

- (1) Suppose that N, for example, refers to an atom whose electron affinity is zero, so that the coefficient b vanishes. Normalization then requires that a be equal to unity and results in

$$V \approx -(O_z N_z : O_z N_z : O_z O_z) = -J_{zz}$$

where the last equality follows from the definition of exchange. In other words, the quantity in parentheses refers to the situation in which two electrons are exchanged back and forth between N and O, whereas the third electron remains stationary on the O atom. Moreover, this interpretation is certainly consistent with the approximation of perfect pairing because the spins are random, in which case we have

$$V \approx 2 \left(-\frac{1}{2} J_{zz} \right) = -J_{zz}$$

- (2) Suppose that N and O now refer to the same type of atom, for example oxygen, so that the coefficients, a and b , are each nearly equal to $(2)^{-1/2}$. The interaction potential then becomes

$$V \approx -J_{zz} \pm (O_z O_z : N_z N_z : O_z N_z)$$

where the last term signifies one electron on one atom, another electron on the other atom, and the third electron equally dividing its time between the two atoms. Thus, this last integral, together with its coefficient (unity in this case), is called a hybrid coulomb-exchange integral, and it clearly provides a measure of the importance of resonance configurations. Also, it is quite obvious from the form of the integrals involved that a good approximation to V should be

$$V \approx -J_{zz} \pm \lambda J_{zz}$$

where λ is a resonance parameter and, in general, depends on the interatomic separation. Vanderslice, Mason, and Maisch (ref. 17) set this quantity equal to a constant, 0.5, but it will be treated here as a variable. The plus sign, of course, refers

to the "extra" electron being in the Π_z orbital and the negative to Π_z^* occupation.

Going back to the original problem of the ground state of nitric oxide, it is certainly to be expected that the resonance parameter, λ , will lie somewhere between its maximum value in case (2), in which the resonance is complete, and its value of zero in case (1). However, we still have to develop a procedure for its calculation.

Since $(O_z O_z : N_z N_z : O_z N_z)$ must be greater than J_{zz} because of overlap considerations, and since λ must vanish whenever a or b is zero, a reasonable functional form seems to be

$$\lambda = \gamma ab$$

where γ in general depends on the interatomic separation and is greater than 2 in the case of complete resonance.

To the extent that γ can be regarded as constant, an assumption which will not be used in our future calculations, its value may be determined by a consideration of the problem described in case (2) above, in which a and b are both nearly equal to $(2)^{-1/2}$. Since this situation implies that the extra electron is just as likely to be found on O as on N, it can be imagined that the contribution of the three-electron bond to the interaction energy of the $(\Pi_z)^2(\Pi_z^*)$ state is

$$-J_{zz} + 2 \left(\frac{1}{2} \right) \left(1 + \frac{1}{2} \right) J_{zz} = \frac{1}{2} J_{zz}$$

that is, $\gamma \approx 3$ (an excellent example is the resonance stabilization of He_2^+).

Proceeding one step further with this idea, it is now possible to derive an expression for the probability (P) of the resonance ionic state $\text{O}^+ - \text{N}^-$. This probability is equal to b^2 and, by using the normalization condition $a^2 + b^2 = 1$, we can write

$$P \approx 1 - a^2$$

where

$$a = \frac{\lambda}{3b} = \frac{\lambda}{3P^{1/2}}$$

Eliminating a and solving the ensuing quadratic equation yields

$$P = \frac{1}{6} \left[3 - (9 - 4\lambda^2)^{1/2} \right] \quad (28)$$

A somewhat better determination of the resonance parameter may be obtained by a consideration of the ground $X^2\Pi$ state of nitric oxide in conjunction with the excited ${}^6\Sigma$ state, which will be described in the next section by use of the delta-function model. The electronic configuration of this latter state is

$$(\sigma_x)(\sigma_x^*)(\Pi_y)(\Pi_y^*)(\Pi_z)(\Pi_z^*)$$

so that the two energies involved are

$$V(^2\Pi) = J_{xx} + \lambda J_{yy} \quad (29)$$

and

$$V(^6\Sigma) = -(1 + \lambda)J_{xx} - 2J_{yy} \quad (30)$$

THE ${}^6\Sigma$ STATE OF NO

A brief study of the potential function given in equation (30), especially when cognizance is taken of the fact that J_{xx} is usually many times greater than J_{yy} in magnitude, clearly indicates that this particular ${}^6\Sigma$ state of nitric oxide is the most repulsive one obtainable from ground state atomic orbitals—at least as long as the interatomic separation is not so small that the coefficients of linear combination of atomic orbitals are effectively different for Π_y and Π_y^* . In addition, it should be noticed that σ type orbitals are emphasized, so that everything seems to point to this being the state most accurately described by a delta-function model with its associated hydrogen-like approximation of taking average electrons.

As pointed out earlier, the situation in the case of heteronuclear molecules is complicated somewhat by the existence of two sets of delta-function strengths and shifting parameters. However, as will be justified later in connection with the treatment of exchange integrals, it is a good approximation to take the geometric mean between corresponding homonuclear molecules, O_2 and N_2 in this problem, in which case the new potential function becomes

$$V(^6\Sigma) = (n_1 n_2)^{1/2} (27.206) g_1 g_2 \exp \left[-\frac{(c_1 \rho_1 + c_2 \rho_2)}{2} \right] \text{eV} \quad (31)$$

where the subscripts 1 and 2 refer to oxygen and nitrogen, respectively; for example, $n_1=6$ and $n_2=5$.

The values of c_i , ρ_i , and g_i are, of course, given

by expressions similar to those in equations (15) and, in particular, values for $c_2 \rho_2$ and g_2 , as well as p , may be obtained from the previous calculations on nitrogen. Since the parameter p depends primarily on the number of electron pairs involved and seems to be fairly insensitive to a small change in this number, the assumption that $p=0.55$ for O_2 as well as N_2 is probably not too bad. Thus, the only additional information needed is the radius of the outermost electron shell of atomic oxygen, defined as the distance at which the electron charge density is a maximum and calculated to be 0.48 Å by use of empirical screening parameters (ref. 20) in Slater atomic orbitals, and the corresponding ionization potential (13.550 eV).

A straightforward calculation, using Newton's iteration procedure to solve equation (15c), yields the results presented in the third column of table V. Also shown in this table is the interaction energy corresponding to the $X^2\Pi$ state, as computed from the Hulburt-Hirschfelder function in equation (27).

THE RESONANCE PARAMETER

It will now be convenient to define a new parameter k as the ratio of exchange integrals J_{xx} to J_{yy} . Equations (29) and (30) may then be written

$$V(^2\Pi) = J_{yy}(k + \lambda) \quad (32)$$

and

$$V(^6\Sigma) = -J_{yy}(k + 2 + k\lambda) \quad (33)$$

Dividing the first by the second and solving for λ yields

$$\lambda = \frac{-[kV(^6\Sigma) + (k+2)V(^2\Pi)]}{V(^6\Sigma) + kV(^2\Pi)} \quad (34)$$

where everything on the right-hand side is known with the exception of k . Notice that λ approaches

TABLE V.—ENERGIES OF THE $X^2\Pi$ AND ${}^6\Sigma$ STATES OF NITRIC OXIDE

r	$X^2\Pi$	${}^6\Sigma$
2.5	-0.1718	0.2693
2.6	-.1307	.2033
2.7	-.1009	.1533
2.8	-.0788	.1156
2.9	-.0621	.0872

zero as k approaches infinity (see table V).

In order to determine this last parameter, use is made of the fact that the exchange energies should, in a major way, be dependent on the corresponding overlap integrals. In fact, a reasonable approximation would appear to be the following:

$$J_{xx} = (\text{O}_x \text{N}_x : \text{O}_x \text{N}_x) \approx \frac{1}{4} S_{xx}^2 [(\text{O}_x \text{O}_x : \text{O}_x \text{O}_x) + (\text{N}_x \text{N}_x : \text{N}_x \text{N}_x) + 2(\text{O}_x \text{O}_x : \text{N}_x \text{N}_x)] \quad (35)$$

$$J_{yy} = (\text{O}_y \text{N}_y : \text{O}_y \text{N}_y) \approx \frac{1}{4} S_{yy}^2 [(\text{O}_y \text{O}_y : \text{O}_y \text{O}_y) + (\text{N}_y \text{N}_y : \text{N}_y \text{N}_y) + 2(\text{O}_y \text{O}_y : \text{N}_y \text{N}_y)] \quad (36)$$

where

$$(\text{O}_x \text{N}_x : \text{O}_x \text{N}_x) = \int [\dots \text{O}_x(1) \text{O}_x(2)]^* H [\dots \text{N}_x(1) \text{N}_x(2)] d\tau, \text{ etc.}$$

H is the complete Hamiltonian operator of the entire molecular system, and S_{ii} is the overlap integral $\int \text{O}_i^* \text{N}_i d\tau$.

Each of the integrals appearing in the right-hand members of equations (35) and (36) represents atomic plus coulombic energies. Since the coulombic energies may be shown to be essentially independent of whether p_x or p_y is used and to constitute only about 0.08 percent of the atomic energies for the distances under consideration, we have to a good approximation (since E_1 is small

compared with E)

$$(\text{O}_x \text{O}_x : \text{O}_x \text{O}_x) \approx (\text{O}_y \text{O}_y : \text{O}_y \text{O}_y) \approx E(\text{O}) + E(\text{N}) + E_1(\text{O}) - E_1(\text{N}) \quad (37)$$

$$(\text{N}_x \text{N}_x : \text{N}_x \text{N}_x) \approx (\text{N}_y \text{N}_y : \text{N}_y \text{N}_y) \approx E(\text{O}) + E(\text{N}) - E_1(\text{O}) + E_1(\text{N}) \quad (38)$$

and

$$(\text{O}_x \text{O}_x : \text{N}_x \text{N}_x) \approx (\text{O}_y \text{O}_y : \text{N}_y \text{N}_y) \approx E(\text{O}) + E(\text{N}) \quad (39)$$

where $E(\text{O})$ and $E(\text{N})$ are the total energies of atomic oxygen and nitrogen, respectively, and $E_1(\text{O})$ and $E_1(\text{N})$ refer to the corresponding one-electron energies. Thus, the expressions for J_{xx} and J_{yy} reduce to

$$J_{xx} \approx S_{xx}^2 [E(\text{O}) + E(\text{N})] \quad (40)$$

and

$$J_{yy} \approx S_{yy}^2 [E(\text{O}) + E(\text{N})] \quad (41)$$

so that

$$k = \left(\frac{S_{xx}}{S_{yy}} \right)^2 \quad (42)$$

The overlap integrals may be evaluated using elliptical coordinates in which the variables are $\mu = (1/r)(r_o + r_N)$, $\nu = (1/r)(r_o - r_N)$, and φ , and where r_o and r_N refer to the distances of an arbitrary point from the nuclei O and N, respectively. The parameter r still represents the internuclear separation and it is also the distance between the foci of the associated ellipse.

Remembering now that r is in angstroms and using the ordinary atomic wave functions, we obtain the following expression for the parameter k :

$$k = \left\{ \frac{\int_1^\infty \int_{-1}^{+1} \int_0^{2\pi} [\nu^4 \mu^2 - \nu^2(\mu^4 + 1) + \mu^2] \exp(-x\mu - y\nu) d\varphi d\nu d\mu}{\int_1^\infty \int_{-1}^{+1} \int_0^{2\pi} [\nu^4(\mu^2 - 1) - \nu^2(\mu^4 - 1) + (\mu^4 - \mu^2)] \exp(-x\mu - y\nu) \cos^2 \varphi d\varphi d\nu d\mu} \right\}^2 \quad (43)$$

where

$$x = [(z_1 + z_2)/4(0.5292)]r = 3.9919r$$

$$y = [(z_1 - z_2)/4(0.5292)]r = 0.3071r$$

z_1 effective nuclear charge seen by an L-shell electron in atomic oxygen (~ 4.55)

z_2 analogous quantity (~ 3.90) for atomic nitrogen

In the case of fairly large internuclear separations, it is obvious from the definition of the elliptical coordinate system, and from the fact that the major contributions to the overlap integrals come from the region roughly half way between the nuclei, that a very reasonable

assumption at this point should be the setting of ν equal to zero. For the purpose of obtaining an idea of the error thus introduced, we shall suppose that the maximum contribution is attained along the line $(1/2)(a_1+a_2)-a_1 \approx 0.04 \text{ \AA}$ to the oxygen side of the geometric center of the molecule. This corresponds to the position of touching of Bohr-type orbits, and the resulting shift will be assumed constant over all greater separations. Assuming, in addition, that the effective magnitude of μ remains of the order of unity, we have the following effects on the integrands of equation (43):

- (1) The value of ν for the above displacement of 0.04 \AA , and for $r=2.7 \text{ \AA}$, is ~ -0.03 . Since the smallest power of ν appearing in the integrands is ν^2 , it is easily seen that this particular effect of the assumption $\nu=0$ is to increase only slightly the values of the overlap integrals.
- (2) The neglect of ν , on the other hand, serves to decrease the values of the overlap integrals through the omission of the factor $\exp(-\gamma\nu) \approx \exp(+0.025)$.
- (3) The exchange integrals are further decreased when full advantage is taken of the geometric mean procedure discussed in connection with equation (31). This implies that the expressions given in equations (40) and (41) should be multiplied by the factor

$$2 \frac{[E(O)E(N)]^{1/2}}{E(O)+E(N)}$$

which is slightly less than unity.

- (4) Finally, the net effect of (1) and (2), only, is to decrease the exchange integrals by a very small amount for the range under consideration. However, as pointed out in a recent paper by the author (ref. 7), and particularly in regard to the supposedly rigorous calculation of the $X^2\Pi$ state, the effective nuclear charges are probably a bit larger than the ones mentioned above. In consequence of this, the exchange integrals should be reduced slightly because of the more compact charge distributions and resulting decrease in overlap. Thus, the elimination of ν is perhaps better for our purposes

than is a direct evaluation of the integrals in equation (43).

In view of the above arguments, the expression for k may now be written

$$k = \left[\frac{2 \int_1^\infty \mu^2 \exp(-x\mu) d\mu}{\int_1^\infty (\mu^4 - \mu^2) \exp(-x\mu) d\mu} \right]^2 \quad (44)$$

or

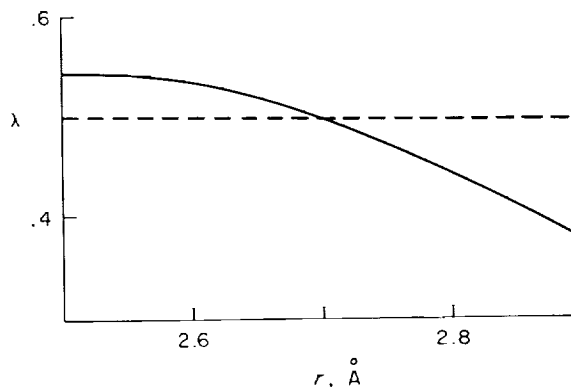
$$k = \left[\frac{(x^4 + 2x^3 + 2x^2)}{(x^3 + 5x^2 + 12x + 12)} \right]^2 \quad (45)$$

As mentioned earlier, the character of the exponentials in equation (44), that is, the form of essentially a product of $\exp(-z_1 r)$ and $\exp(-z_2 r)$, justifies to a large extent the use of the geometric mean in the delta-function model in preference to the arithmetic average.

The results for the resonance parameter, λ , as calculated from equation (34) using equation (45), are presented in table VI and shown graphically in sketch (d). A comparison with the $\lambda=0.5$ assumption of Vanderslice, Mason, and Maisch (ref. 17) is also indicated.

TABLE VI. THE RESONANCE PARAMETER FOR NO AND ASSOCIATED PROBABILITY

r	λ	P
2.5	0.5474	0.0345
2.6	.5363	.0331
2.7	.5016	.0288
2.8	.4495	.0230
2.9	.3860	.0168



Sketch (d).—Resonance parameter for NO.

Also shown in table VI is the probability of the resonance state $O^+ - N^-$, as computed from equation (28). Its small magnitude further justifies our use of equations (32) and (33), without any ionic contributions, and explains the validity of the Hulburt-Hirschfelder curve fit in connection with the ground state. At the same time, since the Hulburt-Hirschfelder function also excludes any ionic effects, we can reasonably postulate that such good fortune will not prevail in the case of diatomic oxygen, where λ is approximately equal to 1.5 and P is correspondingly much larger. These ideas have been confirmed in recent calculations on O_2 by the theoretical group at the University of Maryland (ref. 21).

A question might reasonably be asked at this point as to why, if the ionic forces are negligible anyway, we even bother to introduce λ into equations (32) and (33). The answer is, of course, in order to have some means of correcting or accounting for the fact that the orbital occupied by the "extra" electron is warped one way or the other, depending upon whether it is an attractive or a repulsive bond, and thereby to include the perhaps much larger effect on the exchange forces. Thus, the use of a resonance parameter without an ionic force is entirely consistent in this problem.

THE ${}^4\Pi$ STATE OF NO

As mentioned previously, Vanderslice, et al. (ref. 17), employ a very approximate method for obtaining the excited ${}^4\Pi$ state of nitric oxide, with the result that a strange hump appears in the potential-energy curve even though no rotation is included. It was, therefore, thought interesting to pursue this question of the existence of an activation energy more thoroughly in the light of the present procedure.

The electronic configuration of the ${}^4\Pi$ state is

$$(\sigma_z)^2(\Pi_y)(\Pi_y^*)(\Pi_z)^2(\Pi_z^*)$$

with the corresponding energy given by

$$V({}^4\Pi) = J_{xx} - (2 - \lambda)J_{yy} \quad (46)$$

or

$$V({}^4\Pi) = J_{yy}(k - 2 + \lambda) \quad (47)$$

Dividing by equation (32), one readily obtains

$$V({}^4\Pi) = V({}^2\Pi) \left(1 - \frac{2}{k + \lambda}\right) \quad (48)$$

The results are given in table VII, together with those of Vanderslice, et al., corresponding to points beyond the negative minimum, and it is seen that the hump has now disappeared.

THE $N_2 - O_2$ INTERACTION

The interaction between nitrogen and oxygen atoms, each of which is a member of its own respective diatomic molecule, has already been discussed and summarized in equation (26), which may now be written

$$V = -\frac{2}{3} J_{yy}(k + 2) \quad (49)$$

Dividing by equation (32) and solving for V , we obtain

$$V = -\frac{2}{3} V({}^2\Pi) \left(\frac{k + 2}{k + \lambda}\right) \quad (50)$$

the results of which are nicely curve fitted by the equation

$$V = V_0 \exp(-ar) \quad (51)$$

The desired interaction between nitrogen and oxygen molecules may now be expressed as a sum of the four atomic interactions, each of which is given in the form of equation (51), the orientation dependence being implicitly included through the four values of internuclear separation. In many instances, however, and if the intermolecular separation is sufficiently large, it is convenient to average (ref. 17) the total interaction energy (Φ)

TABLE VII. - THE $V(r)$ INTERACTION FOR THE ${}^4\Pi$ EXCITED STATE OF NITRIC OXIDE

r	Ref. 17	Eq. (48)
2.5	0.0488	-0.1657
2.6	.0453	-.1265
2.7	.0376	-.0979
2.8	.0288	-.0767
2.9	.0207	-.0606

over all orientations to obtain

$$\Phi(R) = 4V_0 \exp(-aR)(a^3 R d_1 d_2)^{-1}$$

$$\left[4(aR+2) \sinh\left(\frac{ad_1}{2}\right) \sinh\left(\frac{ad_2}{2}\right) - 4\left(\frac{ad_1}{2}\right) \sinh\left(\frac{ad_2}{2}\right) \cosh\left(\frac{ad_1}{2}\right) - 4\left(\frac{ad_2}{2}\right) \sinh\left(\frac{ad_1}{2}\right) \cosh\left(\frac{ad_2}{2}\right) \right] \text{ ev} \quad (52)$$

where

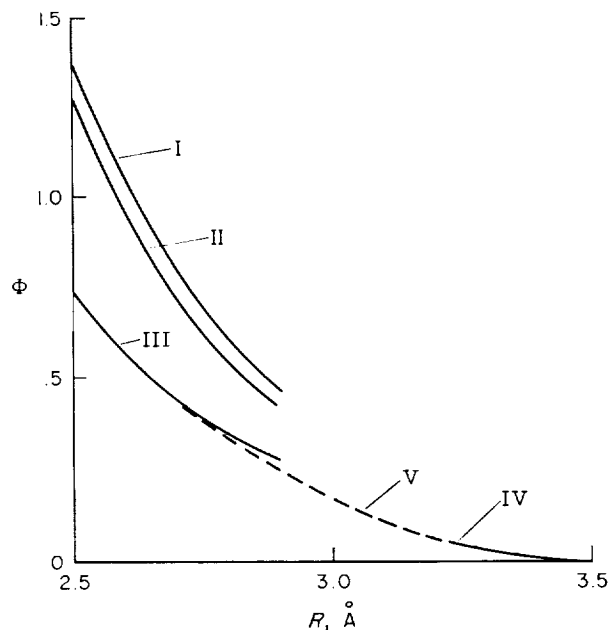
R distance in angstroms between the centers of mass of the molecules

d_1, d_2 bond lengths of O_2 and N_2 , respectively, that is, 1.207398 and 1.094 Å (ref. 13)

This equation yields the results shown in table VIII and plotted as curve III in sketch (c). Also

TABLE VIII.—INTERACTION ENERGIES FOR THE N_2-O_2 SYSTEM

R	Eq. (52)	Eq. (53)
2.5	0.7377	0.7287
2.6	.5654	.5692
2.7	.4396	.4446
2.8	.3457	.3473
2.9	.2741	.2713



Sketch (c).—Comparisons of N_2-O_2 interaction energies.

shown, for purposes of comparison, are the two computations of Vanderslice, Mason, and Maisch (ref. 17), both with (curve II) and without (curve I) the addition of the second-order London dispersion energy. The broken curve (V) is simply a graphically constructed connection between the present results and curve IV, which was derived (ref. 17) from measurements of the viscosities of diatomic nitrogen and oxygen at high temperatures. Finally, as illustrated in column 3 of table VIII, a fairly good approximation to equation (52) is given by the exponential formula

$$\Phi'(R) = A \exp(-BR) \text{ ev} \quad (53)$$

where A and B have the values 350.3 and 2.470, respectively.

As is evidenced by the somewhat greater consistency of curve III with the one derived from high-temperature-gas viscosity data and the relatively greater ease with which the gap can be covered by a reasonable interpolation, the present procedure of using the delta-function model, a variable resonance parameter, and the ratio of exchange integrals would seem to be preferable to that of previous calculations. A somewhat different analysis of the introduction of the parameter k will be presented below in connection with O_2-O_2 .

The procedure of Vanderslice, Mason, and Maisch, however, does present a reasonable first approximation and, in consequence of the fewer equations involved, may prove quite useful in dealing with more complicated species. In particular, the choice of 0.5 for λ is just about as good as can be obtained within the limitations imposed by the assumption that it is independent of internuclear separation. The principal blame for the discrepancies between curves II and III in sketch (c) probably lies in the fact that the range covered in the N_2-O_2 calculation falls precisely in the region of the hump in the 4II state of nitric oxide, which state plays such a vital role in the Vanderslice, et al., method.

It is, on the other hand, difficult to assess the absolute accuracy of the present calculations because of the lack of experimental scattering data to determine the potential curve at smaller separations. Its justification must depend to a large extent on the fact that the procedure involved is

basically the same as that of the previous treatment of N_2-N_2 , for which scattering data were available and with which excellent agreement was obtained. Indeed, the observable variations (e.g., the divergence of curve III from curve V resulting from the neglect of dispersion forces) may be explained in a similar fashion to the explanation of the variations connected with the N_2-N_2 problem. Moreover, a very interesting observation on curves I and II at 2.9 Å indicates that their difference is very close to what is needed to make curve III coincide with V, that is, the simple London dispersion energy may be added to the present results to obtain the complete potential curve beyond this point.

OXYGEN INTERACTIONS

METHOD

The interaction energy between two oxygen molecules will now be determined in much the

same manner as in the previous calculations on N_2-N_2 and N_2-O_2 . Again, because of the compact charge distributions, O^+-O^- resonance (three-electron bonds) between atoms belonging to different O_2 molecules will be ignored. There remains then the following set of nine possibilities:

Oxygen atom (molecule A)						Oxygen atom (molecule B)					
Number of electrons in—						Number of electrons in—					
P_x	P_y	P_z	P_x	P_y	P_z	P_x	P_y	P_z	P_x	P_y	P_z
2	1	1	1	2	1	2	1	1	1	1	2
2	1	1	1	1	2	1	2	1	2	1	1
2	1	1	1	1	2	1	1	2	1	2	1
1	2	1	1	1	2	2	1	1	1	1	2
1	2	1				1	2	1			

A straightforward application of the approximation of perfect pairing to each of these configurations yields, since the spins are random,

$$V(r) = -\frac{1}{9} \left[\left(2J_{xx} + \frac{1}{2}J_{yy} + \frac{1}{2}J_{zz} \right) + \left(J_{xx} + J_{yy} + \frac{1}{2}J_{zz} \right) + \left(J_{xx} + \frac{1}{2}J_{yy} + J_{zz} \right) + \left(J_{xx} + J_{yy} + \frac{1}{2}J_{zz} \right) \right. \\ \left. + \left(\frac{1}{2}J_{xx} + 2J_{yy} + \frac{1}{2}J_{zz} \right) + \left(\frac{1}{2}J_{xx} + J_{yy} + J_{zz} \right) + \left(J_{xx} + \frac{1}{2}J_{yy} + J_{zz} \right) + \left(\frac{1}{2}J_{xx} + J_{yy} + J_{zz} \right) \right. \\ \left. + \left(\frac{1}{2}J_{xx} + \frac{1}{2}J_{yy} + 2J_{zz} \right) \right] \quad (54)$$

where the x direction is taken to coincide with the line of nuclear centers.

On setting $J_{yy} = J_{zz}$ as a consequence of axial symmetry, this equation may be reduced to

$$V(r) = -\frac{8}{9} (J_{xx} + 2J_{yy}) \quad (55)$$

There remains now only the task of eliminating J_{xx} and J_{yy} from equation (55) in order to specify uniquely this interaction. As mentioned previously, however, the ground $X^3\Sigma_g^-$ state of O_2 cannot be used for this purpose because of the inability of a Hulburt-Hirschfelder function to cope with the O^+-O^- resonance phenomenon arising from three-electron bonds; that is, the use of this empirical function would yield a potential curve lying above the correct one. In fact, the only diatomic state, and there are 18 (ref. 22)

which can dissociate into normal (3P) atoms, for which such an empirical function appears to be rigorously confirmed by a Rydberg-Klein-Rees calculation (spectroscopic data) is (ref. 21)

$$^3\Delta_u: (\sigma_x)^2 (\Pi_y)^2 (\Pi_y^*)^2 (\Pi_z) (\Pi_z^*)$$

where the two three-electron bonds of

$$X^3\Sigma_g^- [(\sigma_x)^2 (\Pi_y)^2 (\Pi_y^*) (\Pi_z)^2 (\Pi_z^*)]$$

have been replaced by one consisting of two electrons and another containing four.

The appropriate equations for this state are

$$V(^3\Delta_u) = 0.9154 [(1 - e^{-\beta})^2 + 0.021247\beta^3 e^{-2\beta} (1 + 1.3282\beta) - 1] \quad (56)$$

where

$$\beta = 5.4637 \left(\frac{r - 1.4804}{1.4804} \right) \quad (\text{Hulburt-Hirschfelder})$$

and

$$V(^3\Delta_u) = J_{xx} - 3J_{yy}$$

(approximation of perfect pairing) (57)

where the four-electron bond has been obtained by means of a straightforward extension of the procedure for the three-electron variety discussed previously in connection with nitric oxide. The result, of course, is that the electrons involved may again be described as belonging to atomic rather than molecular orbitals and with a contribution (random spins) of $4(\frac{1}{4} - \frac{3}{4})J_{yy} = -2J_{yy}$ to the interaction potential. The question of resonance thus does not enter this discussion.

Finally, a delta-function computation performed on an excited $^5\Pi_g$ state of O_2 is used to complete the aforementioned O_2-O_2 requirements in the long-range "tail" region.

As a further check on the validity of the above representation of the $^3\Delta_u$ state, since there is some uncertainty in the numbering of the vibrational levels (ref. 21), a second calculation was performed using the $^1\Delta_g$ state as a basis. Despite the fact that the Rydberg-Klein-Rees curve for this state is not known over a large enough range to furnish a stringent test of the fit of an empirical potential, it is believed that the Hulburt-Hirschfelder function should suffice because of the following two- and four-electron bond structures:

$$^1\Delta_g: (\sigma_x)^2 (\Pi_y)^2 (\Pi_z)^2 (\Pi_x)^2$$

The equations corresponding to (56) and (57) are

$$V(^1\Delta_g) = 4.230[(1 - e^{-\beta})^2 + 0.089501\beta^3 e^{-2\beta}(1 + 2.6976\beta) - 1] \quad (58)$$

where

$$\beta = 3.4203 \left(\frac{r - 1.2155}{1.2155} \right)$$

and

$$V(^1\Delta_g) = J_{xx} - J_{yy} \quad (59)$$

Altogether four determinations of $V(r)$ were made and they may be summarized as follows:

1. $^3\Delta_u$ (Hulburt-Hirschfelder) and $^5\Pi_g$ (delta-function model) states of O_2
2. $^1\Delta_g$ (Hulburt-Hirschfelder) and $^5\Pi_g$ (delta-function model) states of O_2

3. $^3\Delta_u$ (Hulburt-Hirschfelder) and $^1\Delta_g$ (Hulburt-Hirschfelder) states of O_2
4. $^5\Pi_g$ (delta-function model) state of O_2 and the ratio of exchange integrals technique. An ulterior motive here is, of course, an investigation of the validity of the introduction of the parameter k in the N_2-O_2 problem. In addition, valuable insight into the limitations of the approximation of perfect pairing should be gained.

THE $^5\Pi_g$ STATE OF O_2

The electronic configuration most appropriate for treatment by a delta-function model is that state in which each valence electron is antibonding to its maximum extent, subject to the condition that the dissociation products are normal atoms. The state most closely fulfilling these requirements appears to be

$$^5\Pi_g: (\sigma_x)(\sigma_x^*)(\Pi_y)(\Pi_y^*)(\Pi_z)(\Pi_z^*)$$

provided the internuclear separation is large enough that the magnitudes of the coefficients of linear combination of atomic orbitals are not effectively different from $2^{-1/2}$.

In the case of complete resonance (homonuclear molecules) it was found previously that the associated resonance parameter (λ) should approach (for small separations) one of the values $\pm 3/2$ for the "extra" electron in a three-electron bond. Actually, this statement is true over the entire range of r as long as one stays within the confines of simple molecular orbital theory; but second-order approximations, namely the introduction of configuration interaction, indicate that $|\lambda|$ should decrease from $3/2$ at large distances. An investigation of these effects is presented in a later section.

Thus, on remembering that a delta-function calculation does not in itself include ionic contributions, we obtain, by application of the approximation of perfect pairing,

$$V(^5\Pi_g) = -\frac{1}{2} (5J_{xx} + 7J_{yy}) \quad (60)$$

The delta-function equations are basically the same as equations (15), except that the ionization potential (13.550 eV), the outermost atomic shell radius (0.48 Å), and the effective number of hydrogen-like electron pairs (6) now refer to

oxygen rather than nitrogen. Again the parameter p in equation (15b) is taken to be 0.55, which might possibly cause the interaction potential to be slightly too high; however, as explained above, this should be of only minor significance. The results of this computation, together with those from equations (56) and (58), are presented in table IX.

THE $V(r)$ INTERACTION

If equations (55), (57), and (60) are combined on the one hand, and (55), (59), and (60) on the other, the interaction between atoms belonging to two different O_2 molecules may be expressed in the following two ways:

$$V(r) = \frac{4}{99} [10V(^5\Pi_g) + 3V(^3\Delta_u)] \quad (61)$$

and

$$V(r) = \frac{2}{9} [2V(^5\Pi_g) + V(^1\Delta_g)] \quad (62)$$

The results, as presented in the second and third columns of table X, are very consistent with each other, thereby indirectly implying that a Hulburt-Hirschfelder function is valid for both the $^3\Delta_u$ and $^1\Delta_g$ states of O_2 .

The remaining two determinations of $V(r)$ are obtained from the combination of equations (55),

TABLE IX. THE $V(r)$ INTERACTIONS FOR $O-O$

r	$^3\Delta_u$	$^1\Delta_g$	$^5\Pi_g$
2.5	-0.0387	0.0854	0.3278
2.6	-.0269	-.0638	.2483
2.7	-.0187	-.0491	.1880
2.8	-.0130	-.0388	.1423
2.9	-.0091	-.0312	.1077

TABLE X. —THE $V(r)$ INTERACTION FOR O_2-O_2

r	Eq. (61)	Eq. (62)	Eq. (63)	Eq. (64)
2.5	0.1278	0.1267	0.1382	0.1179
2.6	.0971	.0962	.1059	.0892
2.7	.0737	.0726	.0842	.0674
2.8	.0559	.0546	.0688	.0510
2.9	.0424	.0409	.0572	.0386

(57), and (59), and from (55) and (60), together with the definition of k in equation (42), as follows:

$$V(r) = \frac{4}{9} [3V(^3\Delta_u) - 5V(^1\Delta_g)] \quad (63)$$

and

$$V(r) = \frac{16}{9} V(^5\Pi_g) \left(\frac{k+2}{5k+7} \right) \quad (64)$$

Since $Z_1=Z_2$ in this case, the equation analogous to (43) becomes

$$k = \left\{ \frac{\int_1^\infty \int_{-1}^{+1} \int_0^{2\pi} [\nu^4 \mu^2 - \nu^2(\mu^4 + 1) + \mu^2] \exp(-x\mu) d\varphi d\nu d\mu}{\int_1^\infty \int_{-1}^{+1} \int_0^{2\pi} [\nu^4(\mu^2 - 1) - \nu^2(\mu^4 - 1) + (\mu^4 - \mu^2)] \exp(-x\mu) \cos^2 \varphi d\varphi d\nu d\mu} \right\}^2 \quad (65)$$

where $x = Zr/2(0.5292)$, and Z is the effective nuclear charge of an L-shell electron in atomic oxygen (~ 4.55).

In contrast to the handling of the nitric oxide problem and because of the fact that y is identically equal to zero, thus making invalid one of the principal arguments in support of setting ν equal to zero, equation (65) was evaluated directly to obtain

$$k = \left(\frac{x^4 + 2x^3 - 3x^2 - 15x - 15}{x^3 + 6x^2 + 15x + 15} \right)^2 \quad (66)$$

Calculations based on equations (63) and (64) are shown as columns four and five of table X,

where it is seen that they are in fairly good agreement with each other and with columns two and three. For example, the deviation between the results of equation (64) and the average of (61) and (62) is only about 7.5 percent, indicating that the ratio of exchange integrals technique is a reasonable approximation whenever sufficient spectroscopic data are not available. A further discussion of this approach is presented in the section "Limitations of the Approximation of Perfect Pairing."

THE RESONANCE PHENOMENON

Since the $^5\Pi_g$ state of O_2 plays the role of a

common denominator in equations (61) and (62), and since the equations agree so well with each other and are at the same time at odds with the results of equation (63), the implications are quite strong that something must be wrong with either the delta-function model or the state chosen to be represented by it.

An obvious first correction would seem to be a reduction in the parameter p of equation (15b); but it has been stated previously that, if anything, p should be greater than the N_2 value of 0.55 in order to approach the correct limit of unity as the atomic number increases. A more direct modification would be perhaps the addition of configuration interaction between states of the same symmetry species to account for the breakdown of simple molecular orbital theory at large separations. This effect is more important here than for $N-N$ and $N-O$ because of the more compact (larger effective nuclear charge) electronic charge distributions of $O-O$. Thus, the distances between atoms need not be as great as before to produce the same molecular orbital deficiencies, a fact confirmed to some extent by the increase in percentage deviation from 8 to 27 between the results of equation (63) and the average of (61) and (62), as r goes from 2.5 to 2.9 Å.

Furthermore, the ${}^5\Pi_g$ state, for example, described in equation (60) should interact to some degree with the configuration

$${}^5\Pi_g: (\sigma_x)^2(\sigma_x^*)(\Pi_y)^2(\Pi_y^*)(\Pi_z)(\Pi_z^*)$$

the existence of which is to be expected on the basis of the incorrect simple molecular orbital prediction that both "extra" electrons might possibly be found on one atom, even at large separations.

Although an exact treatment of this problem is beyond the scope of the present paper, it is nevertheless apparent that the need for configuration interaction may be roughly satisfied by the introduction of a variable resonance parameter ($|\lambda| < 3/2$ and decreasing with increasing separation) into equation (60); that is,

$$V({}^5\Pi_g) = -(1+\lambda)J_{xx} - (2+\lambda)J_{yy} \quad (67)$$

where it is assumed that the λ associated with the x direction is not far different from that associated with y .

A simultaneous solution of this equation with

(57) and (59) then yields

$$\lambda = \frac{V({}^5\Pi_g) - \frac{1}{2}[3V({}^3\Delta_u) - 5V({}^1\Delta_g)]}{V({}^3\Delta_u) - 2V({}^1\Delta_g)} \quad (68)$$

The results, as given in table XI and plotted in sketch (f), are of the predicted order of magnitude, and the general behavior is seen to resemble very closely that of the nitric oxide calculations of sketch (d). The variation in the latter, however, is smaller than that of equation (68) because, for example, of the existence of only one three-electron antibond in the ${}^6\Sigma$ state of NO. Consequently, conversion of this to a three-electron bond, as is done in the O_2 (${}^5\Pi_g$) state above, would further imply a change from approximately "gerade" to "ungerade" symmetry. This results in smaller off-diagonal interaction matrix elements.

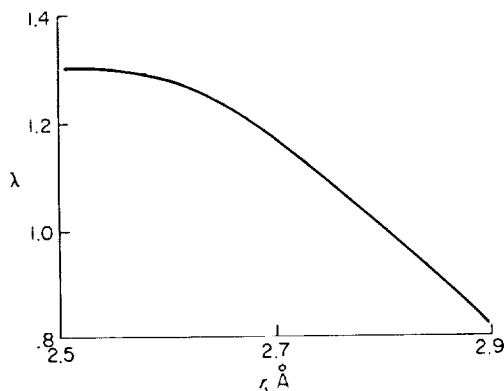
Indeed, these agreements should prove quite influential in any future attempt to corroborate the initial assumptions.

LIMITATIONS OF THE APPROXIMATION OF PERFECT PAIRING

A determination of the parameter k from the ${}^3\Delta_u$ and ${}^1\Delta_g$ states of O_2 furnishes an excellent

TABLE XI.—THE O_2 RESONANCE PARAMETER, λ

r	Eq. (68)
2.5	1.3049
2.6	1.2828
2.7	1.1718
2.8	1.0044
2.9	.8147



Sketch (f).—Resonance parameter for O_2 .

example of the limitations of the approximation of perfect pairing. The simultaneous solution of equations (57) and (59), in conjunction with the definition of k , yields

$$k = \frac{V(^3\Delta_u) - 3V(^1\Delta_g)}{V(^3\Delta_u) - V(^1\Delta_g)} \quad (69)$$

the results of which are found in table XII, together with those from equation (66), for purposes of comparison.

The order of magnitude discrepancies, as well as the obviously incorrect decrease in k with increasing r , may be most easily explained in terms of the following three examples:

- (1) In the usual case of using the approximation of perfect pairing to find the relation between three different states of a molecule, the equations involved are of the general form

$$V_1 = aJ_{xx} + bJ_{yy} + F_1$$

$$V_2 = cJ_{xx} + dJ_{yy} + F_2$$

$$V_3 = eJ_{xx} + fJ_{yy} + F_3$$

where F_i represents the corrections due to Weinbaum type (ref. 23) ionic terms, etc., in the wave function. It is then assumed that these corrections are small enough that they effectively cancel out in the equation of V_3 , possibly, as a linear combination of V_1 and V_2 ; or in other words, the corrections add in the same fashion as the exchange terms. The truth of these assertions is difficult to ascertain, although such seems to be the situation in the N_2 problem. On the other hand, this example may be too simple for any adequate judgment.

TABLE XII.—THE RATIO OF EXCHANGE INTEGRALS, k

r	Eq (66)	Eq. (69)
2.5	52.56	4.655
2.6	58.71	4.455
2.7	65.22	4.227
2.8	72.10	4.009
2.9	79.33	3.820

- (2) Another technique in which this approximation might be employed is that of determining the relation between V_1 , V_2 , and k , where the latter is obtained by means of an independent calculation. The appropriate equation in this case is

$$\frac{V_1}{V_2} = \frac{ak + b + (F_1/J_{yy})}{ck + d + (F_2/J_{yy})} \approx \frac{ak + b}{ck + d}$$

provided k is large enough that the correction terms are insignificant in comparison. The agreement of the previous N_2-O_2 curve with one obtained from high-temperature-gas viscosity data seems to justify this approach, at least insofar as states for which the ionic contribution is known to be of minor importance are concerned.

- (3) Finally, in the example of this section, k is found solely from the relation between V_1 and V_2 , but under the same general restrictions that apply in case (2). The ionic F functions associated with the $^3\Delta_u$ and $^1\Delta_g$ states of O_2 , while apparently not strong enough to affect critically the Hulburt-Hirschfelder descriptions, nevertheless are not so weak as to be negligible in the computation of k . In contrast to the ground state, where conversion of the two three-electron bonds to antibonds results in a quite different energy and ordinary empirical curve fits are not possible, the corresponding $^3\Delta_u$ and $^1\Delta_g$ configuration interaction states have the same valence bond energy as their counterparts. These are, respectively,

$$^3\Delta_u: (\sigma_x^*)^2(\Pi_y)^2(\Pi_y^*)^2(\Pi_z)(\Pi_z^*)$$

$$V = J_{xx} - 3J_{yy}$$

and

$$^1\Delta_g: (\sigma_x^*)^2(\Pi_y)^2(\Pi_y^*)^2(\Pi_z^*)^2$$

$$(\sigma_x^*)^2(\Pi_y)^2(\Pi_y^*)^2(\Pi_z)^2$$

$$(\sigma_x)^2(\Pi_y)^2(\Pi_y^*)^2(\Pi_z^*)^2$$

$$V = J_{xx} - J_{yy}$$

Hence configuration interaction, together with its implied decrease in ionic forces,

is much more important for the latter O_2 excited species.

In spite of these uncertainties, the O_2-O_2 interaction in the following section was computed on the basis of equation (63). A more valid representation, although not enough information is available to evaluate all the unknown parameters, is

$$V(r) = \frac{4}{9} [3V(^3\Delta_u) - 5V(^1\Delta_g) + 5F(^1\Delta_g) - 3F(^3\Delta_u)]$$

where the condition for the recovery of (63) is easily seen to be

$$F(^1\Delta_g) = \frac{3}{5} F(^3\Delta_u)$$

The validity of our procedure must, therefore, rest on whether or not the three $^1\Delta_g$ configuration interaction states effectively lower the ionic contributions below those corresponding to $^3\Delta_u$. Such an occurrence does not seem too unreasonable in view of our present knowledge.

In summary, the usefulness of the approximation of perfect pairing lies in its ability to yield linear relations between potentials corresponding to several different states. Any other application, such as an attempt to analyze the component parts of a particular state or to calculate the energy directly, must be carried through only with the most extreme caution.

THE O_2-O_2 INTERACTION

Curve fitting the results of equation (63) by means of an exponential function, and then averaging the total O_2-O_2 interaction energy over all orientations according to equation (20), where the London dispersion energy must be omitted and $d=1.207398 \text{ \AA}$ for the bond length of ground state O_2 , one obtains the potential values given in column 2 of table XIII. The results tabulated in column 3 were computed from the associated expression

$$\Phi'(R) = 146.6 \exp(-2.109R) \quad (70)$$

and it is seen that the agreement here is to about one significant figure. Finally, column 4 of this table represents the high-temperature-gas viscosity data (ref. 17) as calculated from the following

TABLE XIII.—THE O_2-O_2 INTERACTION ENERGY

R	$\Phi(R)$	$\Phi'(R)$	$\Phi''(R)$
2.5	0.7757	0.7532	
2.6	.5999	.6100	
2.7	.4812	.4941	
2.8	.3963	.4001	
2.9	.3314	.3241	
3.2			0.0246
3.3			.0069
3.4			-.0030
3.5			-.0082

modified Buckingham (exp-6) function (ref. 24):

$$\Phi''(R) = \frac{\epsilon}{1-(6/\alpha)} \left[\frac{6}{\alpha} e^{\alpha(1-\frac{R}{R_m})} - \left(\frac{R_m}{R} \right)^6 \right] \quad (71)$$

where

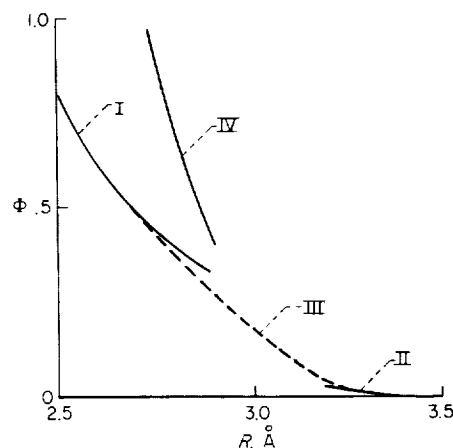
ϵ depth of the Van der Waals minimum (0.01137 ev)

R_m position of this minimum (3.726 \AA)

α dimensionless parameter measuring the steepness of the repulsive energy (17.0)

It is estimated from the temperature range of the viscosity experiments that this curve is not valid for distances smaller than about 3.2 \AA .

In sketch (g) are plotted the results of the present paper (I), together with those from the viscosity measurements (II), and the ease with which the gap between the two regions can be covered by a reasonable interpolation (III) is quite apparent. The divergence between curves I and III in the neighborhood of 2.9 \AA may again be attributed to



Sketch (g).—Comparisons of O_2-O_2 interaction energies.

the neglect of dispersion contributions, effects which are more important here than in the previous examples because of the smaller cutoff distance arising from the interpenetration of more closely packed charge distributions.

Also shown in sketch (g) is a curve (IV) derived from vibrational relaxation time data (refs. 25-29), this being the only experimental information available in the region covered by the present theory. An analysis of vibrational deactivation theory shows that the discrepancies between curves I and IV are to be expected on the basis that the latter is a one-dimensional treatment involving only the end-to-end molecular configuration. This geometry is chosen, of course, because of the maximum energy transfer on collision from vibration to translation; however, it also represents the largest interaction energy of any molecular orientation and should not strictly be compared with the random situation covered here. An additional basic defect of the vibrational theory, as pointed out by Cottrell and Ream (ref. 30), is that the slope of the true interaction curve is not nearly as large as that of the theoretical one, an observation which is clearly borne out in this example.

The recent calculations of Vanderslice, Mason, and Maisch (ref. 21) have been omitted from the above comparisons because of essentially the same reasons discussed in the preceding paragraph. In effect then, any absolute confirmation of the behavior of curve I must await the performance of a suitable scattering experiment.

A final rather interesting observation is that the N_2-N_2 repulsive curve is generally lower than the one corresponding to O_2-O_2 . Thus, the effect of the existence of one more electron pair in any O-O type of interaction seems to overshadow the fact that the electronic charge distribution of nitrogen is less compact and thereby results in greater individual repulsive overlap. The N_2-O_2 curve, on the other hand, tends to lie slightly lower than either of the above in the short-range region ($<2.6 \text{ \AA}$) because the overlap between similar transverse orbitals A and B on atoms of different species is generally smaller than that between orbitals A-A or B-B at the same separation.

AMES RESEARCH CENTER,
NATIONAL AERONAUTICS AND SPACE ADMINISTRATION,
MOFFETT FIELD, CALIF., Sept. 25, 1959.

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